Preprint
UCRL-JC-140499

Type I Frequency Doubling at 1064 nm in $LaCa_4O(BO_3)_3$ (LaCOB), $GdCa_4O(BO_3)_3$ (GdCOB), and $YCa_4O(BO_3)_3$ (YCOB)

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This article was submitted to Advanced Solid State Lasers 2001 Sixteenth Topical Meeting and Tabletop Exhibit, Seattle, Washington, January 28-31, 2001

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March 7, 2001

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Abstract: We have grown and characterized LaCOB, a new member to the GdCOB family of nonlinear crystals. LaCOB has a d_{eff} of 0.52 ± 0.05 pm/V and an angular sensitivity of 1224 ± 184 (cm-rad)$^{-1}$ for type I frequency doubling at 1064 nm. The $d_{\alpha\beta\beta}$ and $d_{\gamma\beta\beta}$ coefficients of the nonlinear optical tensor for LaCOB, GdCOB, and YCOB were determined to have values of |0.26 ± 0.04| pm/V and |1.69 ± 0.17| pm/V, respectively. Results of phase-matching angle measurements at 1064 nm and 1047 nm predict LaCOB to be non-critically phase-matched (NCPM) at 1042 ± 1.5 nm. We also estimate the thermal sensitivity of LaCOB to be less than 0.1 (cm-^{o}C)$^{-1}$.
OCIS codes: (190.0190) Nonlinear optics; (190.4400) Nonlinear optics, materials; (190.2620) Frequency conversion

Introduction

The gadolinium calcium oxyborate (GdCOB) [1-4] type crystals combine many of the best aspects of both KTP [5] and LBO [6] for sum frequency generation of near infrared wavelengths. In a structure such as GdCOB, in which the gadolinium ion can be exchanged for other lanthanide ions, it is possible to alter the birefringence, and thus alter the non-critical phase-matching (NCPM) wavelength. An examination of ionic radius vs. non-critical wavelength for GdCOB and YCOB indicates that as the ionic radius of the lanthanide ion increases the non-critical wavelength tends to shift towards longer wavelengths. This shift in wavelength is due in part to a decrease in the partial birefringence relevant for type I phase-matching. The shift in wavelength is significant: the NCPM wavelength for YCOB for propagation down the γ (Z) dielectric axis is ~840 nm, while that for GdCOB is ~968 nm. A desired point of operation would be a non-critical wavelength range spanning the near infrared (1.03 – 1.064 microns), coincident with the wavelengths available from Yb and Nd doped YAG, YLF, and S-FAP. The logical extreme of this process of lanthanide exchange is to attempt to substitute the largest ionic radius, transparent, lanthanide into the existing crystal structure. To test this hypothesis we grew crystals of LaCOB. In support of our hypothesis, we found that the type I non-critical wavelength of LaCOB is indeed shifted to longer wavelengths. The phase-matching wavelength as a function of angle from the n_γ dielectric axis for second harmonic generation (SHG) is shown in Fig. 1 for LaCOB, GdCOB, and YCOB. LaCOB has a smaller birefringence compared to GdCOB and YCOB, allowing NCPM near 1047 nm.

Crystal Growth and Structure of LaCOB

Boules of LaCOB were grown from a melt using the Czochralski method. Large crack-free crystals are obtained through careful alignment of the seed crystal along the preferred growth direction (the β dielectric axis). The material melts congruently with a growth rate of 1mm/hr from a 3 inch high x 3 inch diameter iridium crucible. Typical growth sizes were 2.5-3.0 cm diameters x 10 cm in length. The crystals were clear, but had small areas with bubble core defects perpendicular to the [010] growth direction. The β dielectric axis was determined using x-ray diffraction and then ~5 mm^3 samples were cut for analysis. The polished faces cut perpendicular to the phase-matching direction were uncoated and had a wedge of approximately 1 degree.

LaCOB is a monoclinic biaxial crystal belonging to the Cm space group. The mutually orthogonal principal dielectric axes in this crystal are labeled (α,β,γ), where α ∥ X, β ∥ Y, and γ ∥ Z relative to (X,Y,Z) given in Ref. 2. We choose this system of description (α,β,γ) as the basis system for our measurements because the α, β, and γ axes can be determined in any crystal relatively simply (using a polariscope) from the orientation of the optic axial plane (the plane containing both optic axes of a biaxial crystal). Standard Laue methods are then used to confirm the orientation to within 0.5 degrees. The refractive indices along the α, β, and γ axes are n_α, n_β, n_γ, respectively, with $n_\alpha<n_\beta<n_\gamma$. Peak phase-matching for type I doubling of 1064 nm light in LaCOB in the α-γ principal plane can be estimated to occur at approximately 80 degrees from the α dielectric axis. The effective nonlinear coefficient for type I SHG for this crystal class in the α-γ principal plane is given by:

$$\boldsymbol{d}_{eff} = \boldsymbol{d}_{\alpha\beta\beta}\sin\phi - \boldsymbol{d}_{\gamma\beta\beta}\cos\phi \qquad (\phi > V_\alpha) \qquad (1)$$

where ϕ is the angle measured from the α dielectric axis in the α-γ plane, $d_{\alpha\beta\beta}$ (d_{xyy} or d_{12}) and $d_{\gamma\beta\beta}$ (d_{zyy} or d_{32}) are coefficients of the nonlinear optical tensor, and V_α is the optic angle measured from the acute bisectrix (ABX).

It should be noted that for propagation down the β dielectric axis, type II non-critical phase-matching for near infrared wavelengths can be achieved using mixed crystals of the type $Gd_xY_{1-x}COB$ (Gd,YCOB). As the crystal is changed from pure GdCOB to pure YCOB, the type II NCPM wavelength range spans from 1200 to 1010 nm. Unfortunately, with a segregation coefficient of 0.89 [7], mixed crystals grown at a particular NCPM wavelength composition will display a variation in the NCPM wavelength along the growth direction. Though this effect will not be significant for the majority of applications requiring 1 cm or smaller apertures, these mixed crystals will not have the uniformity necessary for moderate aperture (5-10 cm) lasers. The effective nonlinear coupling for this type II NCPM process depends upon a single coefficient, $d_{\alpha\gamma\alpha}$ (d_{xzx} or d_{15}).

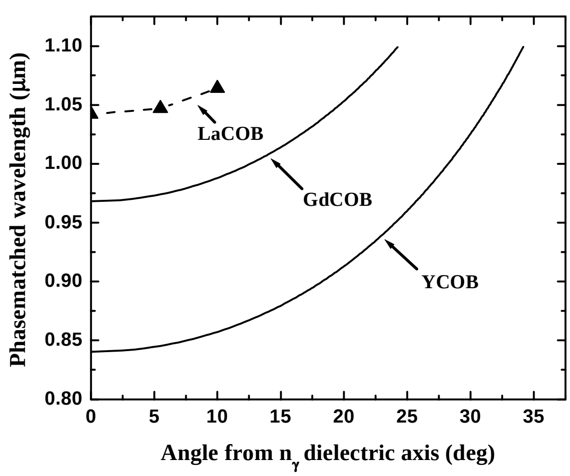

Fig. 1. The change in type I phase-matched wavelength is shown as a function of angle from the n_γ dielectric axis in the α-γ plane for LaCOB, GdCOB, and YCOB. The two points for LaCOB at 5° and 10° were experimentally measured from which the point at 0° was extrapolated, implying that LaCOB will NCPM at approximately 1042 nm.

From the measurements given in Ref. 2, it can be determined apriori that the effective coupling for this type II process will be moderate (1/3 that of the d_{eff} measured for the type I process). However, for the type I process in the α–γ plane, given the contribution to d_{eff} from two coefficients as shown in Eq. (1), the magnitude of the nonlinear coupling coefficient for propagation down the γ dielectric axis cannot be determined from previous measurements performed on YCOB and GdCOB. Aside from the value of determining the relative magnitude of these individual coefficients, thus allowing a determination of the nonlinear coupling for arbitrary wavelengths, it was the hope of the authors that the coupling for type I would be significantly larger than for type II.

Frequency Doubling Experiments

Crystal samples

GdCOB, YCOB, Gd,YCOB, and LaCOB crystals were compared to the standard, well characterized suite of nonlinear optical crystals (BaB_2O_4 (BBO), LiB_3O_5 (LBO), KH_2PO_4 (KDP), and $KTiOPO_4$ (KTP)). Table 1 lists eight of the crystals that were studied. For the biaxial crystals, the angle ϕ is measured from the ABX and the angle θ is measured from the β dielectric axis. In the uniaxial crystals, ϕ is measured from the X axis and θ is measured from the optical axis. The KTP sample (Crystal Associates, NJ) was a commercially produced and coated crystal used as a reference standard to make a relative calculation of d_{eff} for the other crystals. The LBO sample (Fujian Castech, PRC) and the 5.09 mm GdCOB sample (Crismatec, France) were also commercially grown and coated. A 15 mm long commercially grown GdCOB sample cut for maximum conversion was subsequently recut and polished, producing a 3.06 mm sample for phase-matching on the opposite side of the α dielectric axis in the α-γ plane. A single 3.75 mm sample of LaCOB was cut from a boule of LaCOB grown by Kathleen Schaffers along the direction in the α-γ plane corresponding to maximum type I doubling at 1064 nm. We purchased a Czochralski grown boule of Gd,YCOB (Crystal Photonics Inc, FL). The Gd to Y ratio (x=0.275) was adjusted to allow type II NCPM at 1064 nm down the β dielectric axis.

Table 1. Nonlinear crystal properties for type I doubling at 1064 nm

Crystal, Phase-matching Type	Length (mm)	Phase-matching Direction (θ,ϕ) (degrees)	d_{eff} (pm/V)	β_θ (cm-rad)$^{-1}$
KTP,II	**5.17**	**(65.7,90)**	**3.2**	**573 ± 56**
LBO,II	**5.43**	**(69.6,90)**	**0.67 ± 0.05**	**562 ± 25**
GdCOB,I	**5.09**	**(90,70)**†	**0.78 ± 0.06**	**2704 ± 156**
GdCOB,I	**3.06**	**(90,-70)**†	**0.38 ± .04**	**2690 ± 161**
YCOB,I	**5.11**	**(90,57)**†	**1.12 ± 0.07**	**4548 ± 277**
YCOB,I	**5.10**	**(90,-57)**†	**0.69 ± 0.05**	**4385 ± 440**
LaCOB,I	**3.75**	**(90,80.1)**	**0.52 ± 0.05**	**1224 ± 184**
Gd,YCOB, II NCPM	**3.06**	**(0,0)**	**0.37 ± 0.04**	**145 ± 36**

†choice of sign is arbitrary

Effective nonlinear coupling and angular sensitivity measurements

The effect of wavevector mismatch on the 2ω intensity for the eight crystals was measured as a function of angle from the phase-matching direction using an experimental technique similar to Ref. 8. The wavevector mismatch, Δk, can be written in terms of the angular sensitivity, β_θ, and the thermal sensitivity, β_T, as $\Delta k = \beta_\theta \Delta\theta + \beta_T \Delta T$. Examples of the data we collected are shown in Fig. 2, and as can be seen, the data reflects clear sinc^2 behavior. The d_{eff} values in Table 1 for all the crystals except KTP were calculated from the ratio [8] of the peak 2ω signal produced by each sample and that of KTP (d_{eff} = 3.2 pm/V [5]). Our d_{eff} value for LBO agrees within 2% of that of Velsko, et al. [8], therefore we believe our method for determining d_{eff} to be very accurate. The maximum d_{eff} values for doubling 1064 nm light in the α-γ principal plane for LaCOB, GdCOB, and YCOB, as can be seen in Table 1, are 0.52 pm/V, 0.78 pm/V, and 1.12 pm/V, respectively. The d_{eff} for NCPM in Gd,YCOB down the β dielectric axis was measured to be 0.37 pm/V. We also measured the variation of the 2ω intensity with angle in the α-γ principal plane for doubling at 1047 nm in LaCOB. The angle for maximum doubling at 1047 nm was 5.5^o from the γ dielectric axis. We determined, for doubling 1047 nm light in LaCOB, a d_{eff} and β_θ of 0.37 ± 0.04 pm/V and 716 ± 107 $(\text{cm-rad})^{-1}$, respectively. From the measurements at 1064 nm and 1047 nm, we estimate the type I NCPM wavelength of LaCOB to be 1042 ± 1.5 nm.

Calculation of absolute nonlinear coefficients

In the GdCOB type crystals, maximum phase-matching occurs for type I interactions in the α–γ principal plane at two propagation directions, ±φ, symmetric about the α dielectric axis. The two sets of d_{eff} values for GdCOB and YCOB in Table 1 allow us to calculate numeric values for $d_{\alpha\beta\beta}$ and $d_{\gamma\beta\beta}$ from Eq. (1).

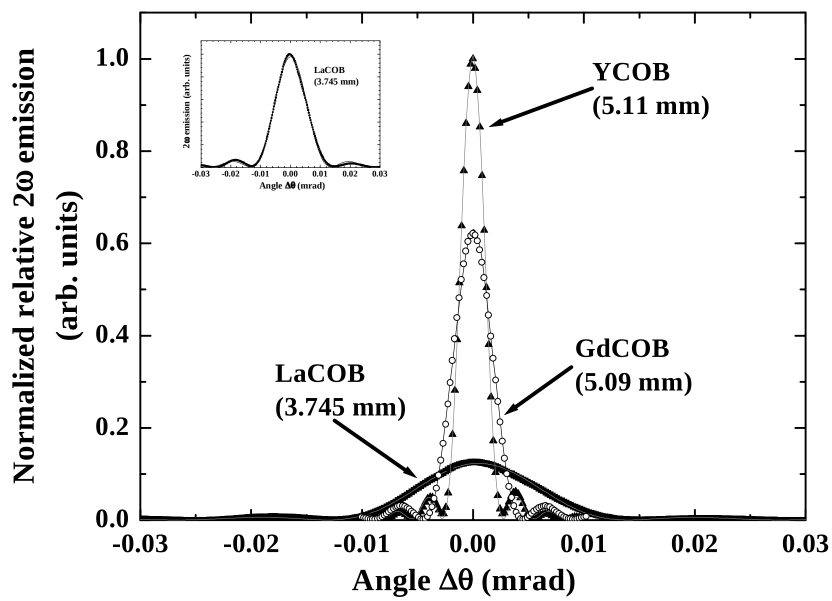

Fig. 2. Normalized 2ω emission for type I doubling at 1064 nm as a function of angle from the maximum phase-matching direction in the α-γ principal plane for LaCOB, GdCOB, and YCOB. The data has been normalized with the peak 2ω value of YCOB. The inset shows the data for LaCOB on an expanded vertical scale that reveals the sinc^2 behavior. The lines through each of the data sets are the corresponding theoretical fits of $(\sin(\Delta kL/2)/\Delta kL/2)^2$. The peak 2ω response of LaCOB is moderate but its angular sensitivity is about one-half that of GdCOB and one-third that of YCOB.

Table 2. Calculated values for $d_{\alpha\beta\beta}$ and $d_{\gamma\beta\beta}$ for type I SHG in GdCOB and YCOB

Crystal	ϕ (α axis)	$d_{\alpha\beta\beta}$(calculated)	$d_{\gamma\beta\beta}$(calculated)
GdCOB	**70°**	**$\|0.22 \pm 0.05\|$ pm/V**	**$\|1.72 \pm 0.13\|$ pm/V**
YCOB	**57°**	**$\|0.26 \pm 0.04\|$ pm/V**	**$\|1.69 \pm 0.17\|$ pm/V**

The values for $d_{\alpha\beta\beta}$ and $d_{\gamma\beta\beta}$ we determine for type I SHG in GdCOB and YCOB are shown in Table 2. The two sets of values for $d_{\alpha\beta\beta}$ and $d_{\gamma\beta\beta}$ for GdCOB and YCOB agree within the experimental uncertainty. These values differ from those found in the literature [9,10]. If the values we derive for YCOB for $d_{\alpha\beta\beta}$ and $d_{\gamma\beta\beta}$ are used in Eq. (1) to calculate the maximum d_{eff} for LaCOB doubling 1047 nm and 1064 nm light we obtain the values shown in Table 3. Notice in Table 3 that the experimental and calculated values for d_{eff} are identical within the experimental errors. From these measurements and calculations, we conclude that the nonlinear optical coefficients, $d_{\alpha\beta\beta}$ and $d_{\gamma\beta\beta}$, are essentially the same, within the measurement uncertainty, amongst GdCOB, YCOB, and LaCOB. Therefore the nonlinear optical coupling for phase-matching in the α-γ principal plane for all three crystals can be determined using the above values with Eq. (1).

Table 3. Experimental and calculated d_{eff} values for doubling 1064 nm and 1047 nm light in LaCOB

Crystal	SHG process	ϕ (α axis)	d_{eff}(experimental)	d_{eff}(calculated)
LaCOB	**1064 nm → 532 nm**	**80.1°**	**0.52 ± 0.05 pm/V**	**0.55 pm/V**
LaCOB	**1047 nm → 523.5 nm**	**84.5°**	**0.37 ± 0.04 pm/V**	**0.41 pm/V**

Thermal sensitivities

We studied the variation of second harmonic generation (SHG) at 532 nm for LaCOB over the temperature range 10-100 °C. Our data revealed that the SHG was essentially constant over this range of temperatures suggesting that peak phase-matching in LaCOB is very thermally insensitive.

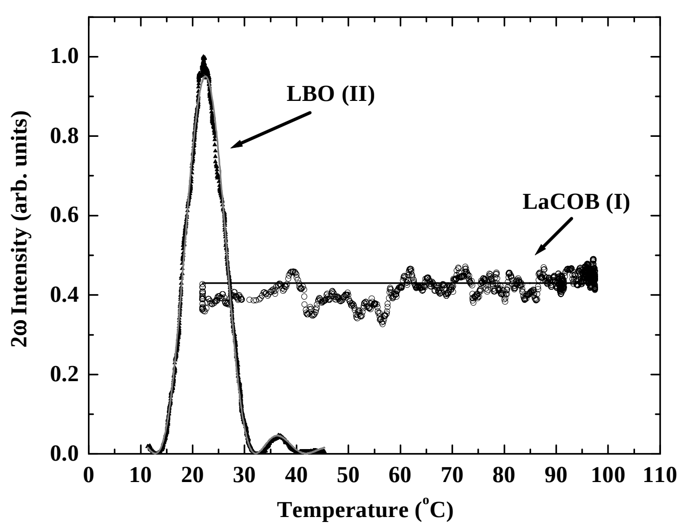

Fig. 3. Variation of 2ω (532 nm) intensity with temperature for type I doubling in LaCOB and type II doubling in LBO. The lines through the data are theoretical fits of $(\sin(\Delta kL/2)/\Delta kL/2)^2$.

The insensitivity of LaCOB over this range of temperatures made it difficult to identify clear $sinc^2$ behavior in our data. We could, however, estimate an upper bound to β_T for LaCOB of 0.1 $(cm\text{-}^oC)^{-1}$. LaCOB, GdCOB, and YCOB exhibited similar temperature insensitivity.

Summary

We have grown and characterized LaCOB, a new member of the GdCOB family of nonlinear crystals. In addition, we have compared and determined the relative nonlinear coupling coefficients of LaCOB, GdCOB, YCOB, and Gd,YCOB to the standard suite of nonlinear optical crystals. We have studied SHG in LaCOB, GdCOB, and YCOB and found that the coefficients of the nonlinear optical tensor for type I SHG in the α-γ principal plane are equivalent within the experimental uncertainty. This implies that the d_{eff} values for these three materials vary primarily due to differences in their birefringence determined only by the phasematching angle within the α–γ plane. The combination of low angular and thermal sensitivities, and moderate effective nonlinear coupling potentially makes LaCOB attractive for intracavity doubling of Yb^{3+}:$Sr_5(PO_4)_3F$ (Yb:S-FAP) lasers, particularly sources in which a moderate aperture (5-10 cm) leads to a requirement of high optical homogeneity.

Acknowledgments

The authors wish to thank J. Embree, K. Kanz, J. Lang, P. Thelin, E. Utterback, and P. Waide, all with the Lawrence Livermore National Laboratory, for their assistance. In addition we would like to thank B. H. T. Chai of Crystal Photonics Inc, FL. This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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